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# **THE HYDROXYL RADICAL REACTION RATE CONSTANT AND PRODUCTS OF CYCLOHEXANOL**

**William R. Bradley, Sheryl E. Wyatt (Calidonna)  
Applied Research Associates  
P.O. Box 40128  
Tyndall AFB, FL 32403**

**J. Raymond Wells, Michael V. Henley, Gina M. Graziano  
Air Force Research Laboratory**

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# The Hydroxyl Radical Reaction Rate Constant and Products of Cyclohexanol

W. R. BRADLEY,<sup>1,a</sup> S. E. WYATT,<sup>1</sup> J. R. WELLS,<sup>2,b</sup> M. V. HENLEY,<sup>2</sup> G. M. GRAZIANO<sup>2</sup>

<sup>1</sup>Applied Research Associates, Gulf Coast Division, P.O. Box 40128, Bldg. 1142, Mississippi Road, Tyndall Air Force Base, FL 32403

<sup>2</sup>Air Force Research Laboratory, Airbase and Environmental Technology Division, AFRL/MLQR, 139 Barnes Drive, Tyndall AFB, FL 32403-5323

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**ABSTRACT:** The gas phase reaction of the hydroxyl radical (OH) with cyclohexanol (COL) has been studied. The rate coefficient was determined to be  $(19.0 \pm 4.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (at  $297 \pm 3 \text{ K}$  and 1 atmosphere total pressure) using the relative rate technique with pentanal, decane, and tridecane as the reference compounds. Assuming an average OH concentration of  $1 \times 10^6 \text{ molecules cm}^{-3}$ , an atmospheric lifetime of 15 h is calculated for cyclohexanol. Products of the OH + COL reaction were determined to more clearly define COL's atmospheric degradation mechanism. The observed products and their formation yields were: cyclohexanone ( $0.55 \pm 0.06$ ), hexanedial ( $0.32 \pm 0.15$ ), 3-hydroxycyclohexanone ( $0.31 \pm 0.14$ ), and 4-hydroxycyclohexanone ( $0.08 \pm 0.04$ ). Consideration of the potential reaction pathways suggests that each of these products is formed via hydrogen abstraction at a different site on the COL ring. The products and their relative amounts are discussed in light of the predicted yields for each reaction channel. © 2001 John Wiley & Sons, Inc. *Int J Chem Kinet* 33: 108–117, 2001

## INTRODUCTION

We have recently reported the results from studies of the gas-phase reactions of several oxygenated species [1–6] and siloxanes [7] with the hydroxyl radical [OH]. In those studies we have tried to present kinetic and product data that can enhance current structure–activity relationships [SAR] used to assess a chemical's environmental impact [8].

In the work presented here, we extend our investi-

gations to cyclohexanol (COL), an important industrial precursor in the production of other ringed species [9]. In the troposphere, most volatile organic compounds (without double and triple bonds) have been shown to react with OH via hydrogen abstraction to form an alkyl radical (R), which then rapidly adds  $\text{O}_2$  to form an organic peroxy ( $\text{RO}_2$ ) radical [10]. In the presence of NO, peroxy radicals react with NO to form the corresponding alkoxy radical plus  $\text{NO}_2$ , together with formation of an organic nitrate [10]. For example, COL has four unique sites for potential hydrogen removal, as shown in Scheme I.

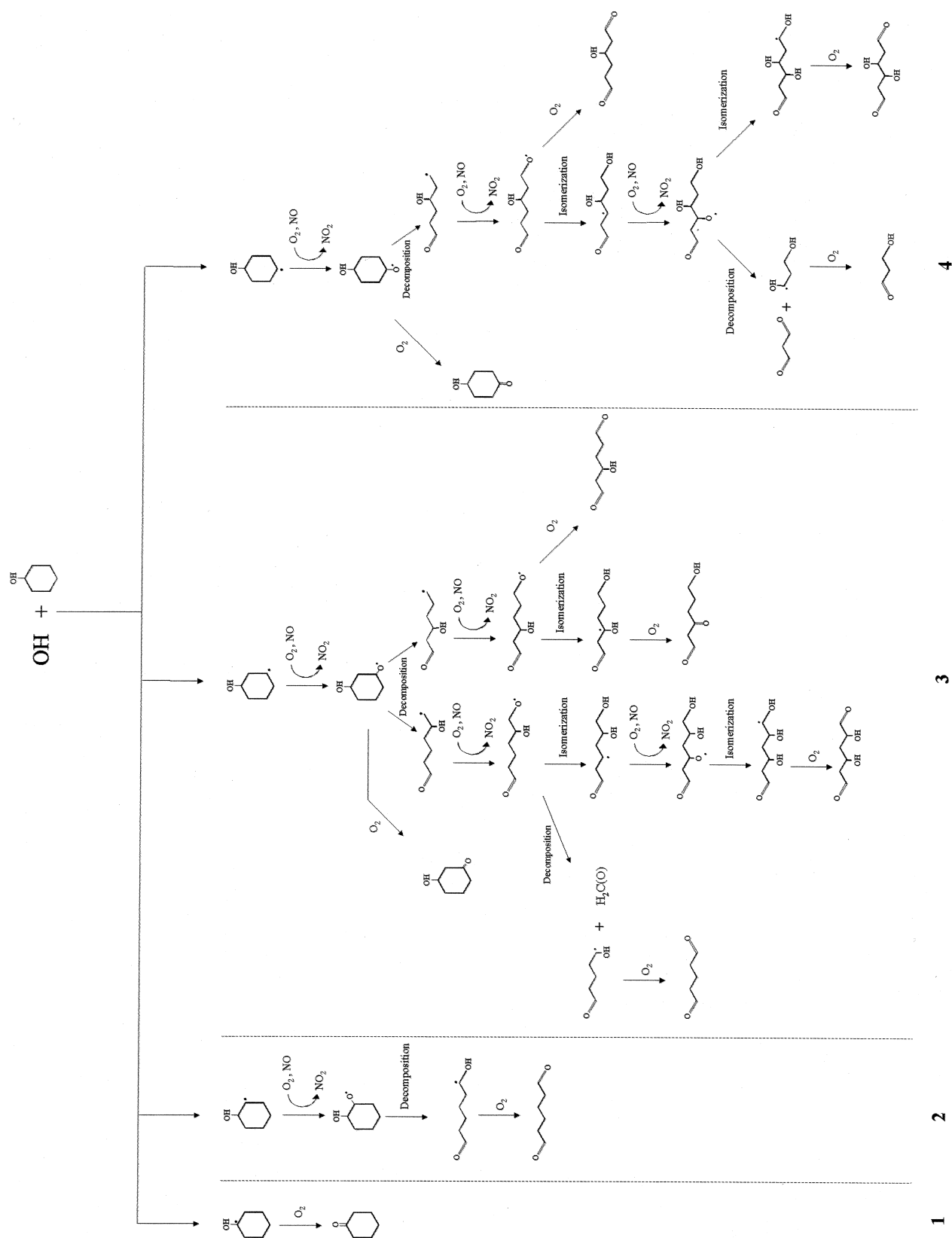
The overall rate of the OH + COL reaction is dependent upon the reaction rate at each abstraction site. The relative contribution from each site and the subsequent reactions of the radicals formed (the reaction channel) determine the quantitative mix of degradation

Correspondence to: S. E. Wyatt (swyatt@ara.com)

<sup>a</sup> Current Address: Department of the Navy, CSS Code A51, 6703 W Hwy 98, Panama City Beach, FL 32407

<sup>b</sup> Current Address: NIOSH, Division of Respiratory Disease Studies, Respirator Branch, 1095 Willowdale Road, Morgantown, WV 26505

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products. In Scheme I, we also depict the expected subsequent reactions of each cyclohexoxy alkoxy radical (with some subsequent reaction pathways being omitted based on estimation of the relative importance of the reactions of certain alkoxy radicals [10, 11]). In this article, we report the overall rate constant of OH with COL as measured by the relative rate method [12]. The observed products of the OH + COL reaction in the presence of NO are reported and used to assess COL's expected atmospheric reaction mechanism. Neither the OH rate constant nor possible reaction mechanisms for COL have been reported previously.

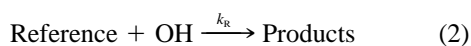
## EXPERIMENTAL

### Reaction Chamber

Kinetic and product determination experiments were conducted with apparatus similar to previous studies [1,3,13,14]. A brief description is provided here. Reactants were introduced and samples were withdrawn through a 6.4-mm Swagelok fitting attached to a 2-mil FEP Teflon®-film bag (50–120 L). Dry compressed air was added as a diluent to the reaction bag and measured with a 0–100 L·min<sup>-1</sup> MKS mass flow controller. The filler system was equipped with a syringe injection port, facilitating the introduction of both liquid and gaseous reactants via the flowing airstream. All reactant mixtures and calibration standards were generated by this system. Irradiations were carried out by placing the reaction bag into a light tight chamber. The chamber employed the following mix of lamps: 6-Philips TL40W/03; 1-GE F40BL; 2-QPANEL UV351; and 7-QPANEL UV340. This lamp mixture approximates solar radiation from 300 to 450 nm.

### Kinetic Rate Method

The experimental procedures for determining the OH + COL reaction kinetics were similar to those described previously [13,14]:



The rate equations for reactions (1) and (2) are combined and integrated resulting in the following equation:

$$\ln\left(\frac{[\text{COL}]_0}{[\text{COL}]_t}\right) = \frac{k_{\text{COL}}}{k_{\text{R}_j}} \ln\left(\frac{[\text{R}_j]_0}{[\text{R}_j]_t}\right) \quad (I)$$

If reaction with OH is the only removal mechanism for COL and reference, a plot of  $\ln([\text{COL}]_0/[\text{COL}]_t)$  versus  $\ln([\text{R}_j]_0/[\text{R}_j]_t)/k_{\text{R}}$  yields a straight line with an intercept of zero and a slope equal to  $k_{\text{COL}}$ . The OH rate constant experiments for COL employed the use of three reference compounds ( $\text{R}_j$ ): decane, tridecane, and pentanal. The use of three different reference compounds with different OH rate constants increases the confidence in the validity of the OH + COL rate constant measured.

Nitric oxide (NO, 99%+ pure obtained from Matheson Gases) was added to facilitate the generation of OH and to minimize ozone ( $\text{O}_3$ ) and  $\text{NO}_3$  formation. Thus the experimental parameters would favor the first OH hydrogen abstraction step with minimal opportunity for side reactions from other radicals.

The typical concentrations of the pertinent species in the reaction bag were 1.4–3.5 ppm COL, 1.2–2.8 ppm reference, 10 ppm  $\text{CH}_3\text{ONO}$ , and 1 ppm NO in air. These mixtures were allowed to stand for 30–60 minutes before initial species concentration ( $[\text{X}]_0$ ) samples were collected. Typically, stepped 3–5 second irradiation intervals were used on the reaction mixture for a combined total photolysis time of approximately 50 seconds.

### Kinetic Study Analysis

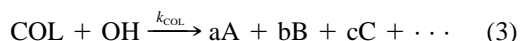
Samples from kinetic studies were quantitatively monitored using a Hewlett-Packard (HP) gas chromatograph (GC) 5890 with a flame ionization detector (FID) or a Mass Selective Detector (MSD) using HP series Chem Station software. The FID signal or total ion chromatogram (TIC) was used to determine COL and reference concentrations. Gas samples for both detectors were cryogenically ( $-65^\circ\text{C}$ ) collected on a Hastelloy C sample loop ( $\sim 1.3$  ml) and injected onto the GC column (Restek Stabilwax-DA, 0.53 mm i.d., 30-m, 1.0  $\mu\text{m}$  film thickness) with a heated rotary valve [15]. The GC temperature program used was as follows:  $45^\circ\text{C}$  for 10 minutes then  $12^\circ\text{C}/\text{min}$  to  $220^\circ\text{C}$  and held for 3 minutes. Helium (UHP grade), the carrier gas, was supplied by Air Products and used as received.

All measurements were at least duplicated. A relative standard deviation (the data set standard deviation divided by the data set average) of approximately 2.5% was achieved with the described sampling method. Several interference experiments were conducted to assure the validity of the OH rate constant.

They consisted of looking for possible chromatographic co-elution of methyl nitrite, NO, reference, COL, and the hydroxyl radical reaction products. Two control experiments were conducted to determine the stability of the reference and COL coexisting in the same bag. First, the reference and COL were injected into the bag, quantified, photolyzed for 6 minutes, and requantified. Second, methyl nitrite, NO, reference, and COL were injected into the bag, quantified, left to sit overnight and then requantified. None of these preliminary experiments yielded chromatographic peak overlaps or observable reactions occurring without photoinitiation. At the end of each run, the Teflon® bag was cleaned by flushing the bag 6 times with air containing <0.1 ppm total hydrocarbon. Measurements of an air-filled bag showed no cross contamination between runs.

### Product Yield Method

The OH radical can theoretically abstract any hydrogen on the COL ring, resulting in multiple products (see Scheme I). Therefore, reaction (1) can be expanded to



A plot of the loss of COL versus the formation of a given product should generate a straight line with a slope equal to the individual product yield and an intercept of zero. However, the OH + COL reaction products could in turn react with OH. Therefore, to obtain more accurate formation yield results the observed product concentrations have to be corrected for OH + reaction product reactions. This correction,  $F$ , has been described in detail [16,17] and has the following form:

$$F = \frac{(k_{\text{COL}} - k_p)}{k_{\text{COL}}} \times \frac{1 - \frac{[\text{COL}]_t}{[\text{COL}]_0}}{\left(\frac{[\text{COL}]_t}{[\text{COL}]_0}\right)^{k_p/k_{\text{COL}}} - \frac{[\text{COL}]_t}{[\text{COL}]_0}} \quad (\text{II})$$

$k_{\text{COL}}$  is the OH + COL rate constant, and  $k_p$  is the rate constant for the reaction of OH with the reaction product.

Conditions for OH + COL reaction product studies were similar to those for reaction rate experiments except that the reference compound was excluded from the reaction mixture and the COL concentration was approximately doubled (4.9–9 ppm).

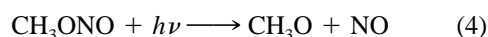
### Product Study Analysis

Reactant mixtures and standards from product identification experiments were sampled by exposing a 100% polydimethylsiloxane solid phase microextraction fiber (SPME) in the reaction bag for 2 minutes. SPME samples were subsequently analyzed with a ThermoQuest Trace 2000 GC combined with a Finnigan GCQ mass spectrometer. Full-scan electron impact ionization spectra were collected from 29 to 250 mass units. The TIC was used to determine COL and product concentrations. A Restek Rtx-1701 column (0.53 mm i.d., 30-m length, 1.0  $\mu\text{m}$  film thickness) provided compound separation. The GC temperature program used was as follows: 35°C for 5 minutes then 6°C/min to 125°C and held for 11 minutes. Helium (UHP grade), the carrier gas, was supplied by Air Products and used as received.

Analysis for carbonyl compounds produced by gas-phase reactions were conducted by flowing 10 L of the reaction bag contents over 2,4-dinitrophenylhydrazine (DNPH)-impregnated cartridges. Hydrazones formed by derivatization were extracted with acetonitrile and quantitatively measured by HPLC (HP 1050) using a three-component gradient solvent program, as described previously [18].

### Chemicals and Reagents

OH, the primary oxidizing radical in the atmosphere, was generated from the photolysis of methyl nitrite ( $\text{CH}_3\text{ONO}$ ) in the presence of nitric oxide (NO) in air [12]:



$\text{CH}_3\text{ONO}$  was prepared in gram quantities using the method of Taylor et al. [19] and stored in a lecture bottle at room temperature. The  $\text{CH}_3\text{ONO}$  purity (>95%) was verified by FT-IR.

All volatile organic compounds were used as received. COL, tridecane, and decane were obtained from Aldrich with a purity of 99%+. Pentanal (99%+) and cyclohexanone (99%+) were purchased through Ultra Scientific. Methanol and acetonitrile, HPLC grade, were received from Aldrich Chemical. The water was distilled, deionized to 18 megaohm, and filtered using a Milli-Q® filter system. Experiments were carried out at  $298 \pm 3$  K at about 1 atmosphere.

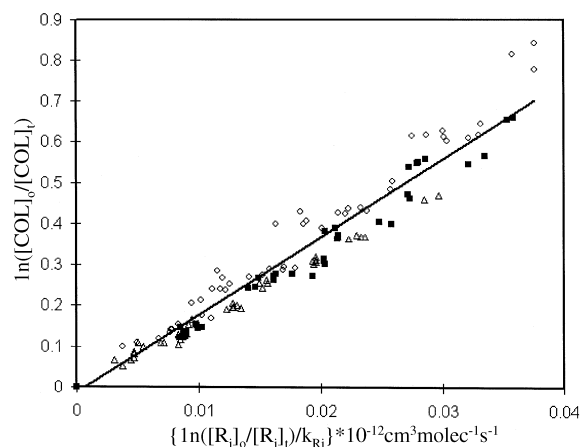
## RESULTS

### OH + COL Reaction Rate Constant ( $k_{\text{COL}}$ )

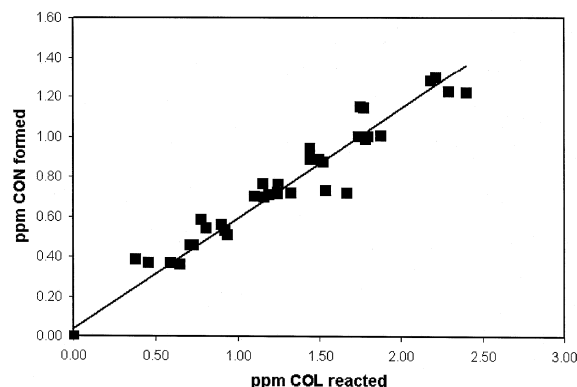
Typically, five experimental runs were conducted on each COL/reference pair. The plot of a modified version of equation (I) is shown in Figure 1. The  $\ln([R_j]_0/[R_j]_t)$  term is divided by the respective reference rate constant (decane  $11.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , tridecane  $16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and pentanal  $28.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) [10] and multiplied by  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , resulting in a unitless number. This yields a slope that is equal to the hydroxyl radical/COL rate constant,  $k_{\text{COL}}$ , divided by  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This modification allows for a direct comparison of the three reference compound/COL data sets.

The combined data result in a slope that yields a hydroxyl radical bimolecular rate constant,  $k_{\text{COL}}$ , of  $(19.0 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The data points at the origin are experimental points because pre-irradiation,  $t = 0$ , data showed no detectable loss of COL or reference. The error in the rate constant stated above is the 95% confidence level from the random uncertainty in the slope. Analysis of the calculated y-intercept shows the value to be not statistically different from zero (95% confidence level). The individual  $k_{\text{COL}}$  values were  $(18.2 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  using tridecane,  $(20.5 \pm 0.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  using decane, and  $(15.7 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  using pentanal.

Incorporating the uncertainties associated with the reference rate constants ( $\pm 25\%$ ) used to derive  $k_{\text{COL}}$ , yields a final value of  $(19.0 \pm 4.8) \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .



**Figure 1** COL relative rate plot with decane (○), pentanal (△) and tridecane (■) as reference compounds. The OH + COL rate constant,  $k_{\text{COL}}$ , measured is  $19.0 \pm 0.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .

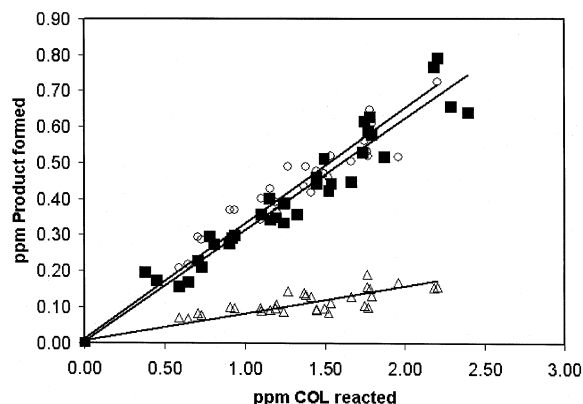


**Figure 2** Plot of COL reacted versus CON formed (■). The slope of the linear least squares analysis with is  $0.55 \pm 0.06$ .

$\text{molecule}^{-1} \text{ s}^{-1}$ . Assuming an  $[\text{OH}] = 1 \times 10^6 \text{ molecules cm}^{-3}$ , the atmospheric (1/e) lifetime calculated for COL is 15 hours. The observed rate constant can be compared with  $k_{\text{COL}} = 17.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , calculated using SAR relationships [8] programmed into the Atmospheric Oxidation Program (AOPWIN v1.89) available from Syracuse Research Corporation. This estimated value is within the error limits of the final value reported here.

### Identification of OH + COL Reaction Products

Cyclohexanone (CON) was the only OH + COL reaction product observed during the initial kinetic experiments. Its presence was also detected later using the DNPH derivatization method described above and confirmed against a commercial standard. HPLC analysis of the DNPH cartridges also indicated at least one other carbonyl product in addition to CON. The unknown product(s) eluted closely to CON, indicating similar size. An intermediate polarity column (Rtx-1701) was selected for further analysis in the system used for kinetics experiments (conditions similar to those ultimately used for the GCQ). Traces of hexanedial (HxD), 3-hydroxycyclohexanone (3HC), and 4-hydroxycyclohexanone (4HC) were detected, but quantitative results were not repeatable ( $<30\%$ ). However, there was sufficient data to allow preliminary compound identifications from the mass spectral data sets by searching the Wiley/NBS Mass Spectra Library. It was thought that the quantitative problems arose from the cryogenic trapping system, so sampling via SPME fiber was substituted. SPME samples were analyzed on the GCQ and the repeatability found to be acceptable ( $<5\%$ ). Identification of each isomer



**Figure 3** Plot of COL reacted versus HXD (○), 3HC (■) and 4HC (△) formed. The slopes of the linear least squares analysis are  $0.32 \pm 0.15$  for HXD,  $0.31 \pm 0.14$  for 3HC, and  $0.08 \pm 0.04$  for 4HC.

was achieved by comparing the spectral and retention time data of the GCQ to that of the GC/MSD (commercial standards of the isomers were not readily available to allow direct confirmation).

Typically, oxygenated organic species react with OH to subsequently generate other oxygenated organic products [1–6,11,20–24]. The reaction products CON, HXD, 3HC, and 4HC are therefore consistent with previously observed products from OH + oxygenated organic species.

The peroxy radicals ( $\text{ROO}\cdot$ ) formed during the reaction pathways are expected to react in the atmosphere with NO to form alkyl nitrates. During our experiments, we found no evidence for the formation of alkyl nitrates.

### OH + COL Product Yield

Table I summarizes the predicted and experimental product yield data for the products of the OH + COL reaction. The observed yields of CON, 3HC, 4HC, and HXD are based on the slope of the COL reacted versus product formed plots (Figs. 2 and 3). The reported error in the product yield is the 95% confidence interval from the random uncertainty in the slope combined with estimated overall uncertainties in the GCQ response factors for COL and each of the products. COL and CON calibration curves were generated for the GCQ using commercial standards. For the product CON, the uncertainty was estimated to be +5%. No commercial standards were readily available for the other products, and so the concentrations of HXD, 3HC, and 4HC were approximated using the calibration curve for COL. The estimated uncertainty in the GCQ response factors for these products was  $\pm 40\%$

each. This was based on the difference in the response observed for commercial standards of COL and CON.

**F**, the correction factor, was multiplied by the product concentration data (in Figs. 2 and 3), resulting in more accurate product yields. The value for  $k_{\text{CON}}$  has been experimentally determined by Dagaut et al. [25] and a value of  $6.39 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was used in equation (II). From equation (II) the average [CON] correction was 1.04 (maximum correction 1.12). From data in Figure 2 and incorporating the error estimates, the yield of CON was determined to be  $0.55 \pm 0.06$ .

As a comparison, using SAR (AOPWIN v1.89),  $k_{\text{CON}}$  was calculated to equal  $12.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The calculated yield for CON when using the SAR value for  $k_{\text{CON}}$  was not statistically different than the value in Table I.

There is currently no experimentally determined  $k_p$  for HXD, 3HC, or 4HC. Using SAR (AOPWIN v1.89),  $k_p$  were estimated for HXD, 3HC, and 4HC as  $52.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ,  $40.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , and  $21.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. From equation (II), the average correction was 1.38 (maximum correction, 2.32) for HXD, 1.28 (maximum correction, 1.96) for 3HC, and 1.14 (maximum correction, 1.45) for 4HC. The following yields were calculated from the plots in Figure 3:  $0.32 \pm 0.15$  for HXD,  $0.31 \pm 0.14$  for 3HC, and  $0.08 \pm 0.04$  for 4HC.

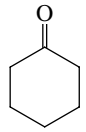
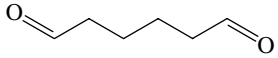
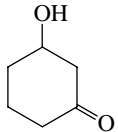
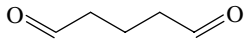
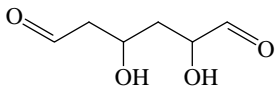
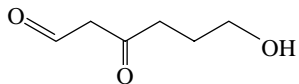
It should be noted that each profile was highly correlated and the intercept found to be not statistically different than zero (95% C.I.). This strongly suggests that no unusual side reactions generated or removed primary reaction products. For completeness, the  $k_p$  values are presented with the respective product in Table I.

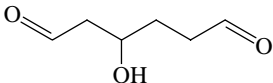
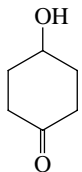
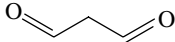
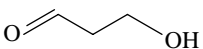
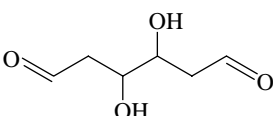
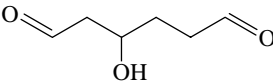
### DISCUSSION

The proposed mechanism for the formation of CON, the principle product observed from the OH + COL reaction, has the radical generated by site 1 abstraction reacting with  $\text{O}_2$  to form CON rather than forming an  $\text{RO}\cdot$  intermediate (see Scheme I). This mechanism is consistent with previously reported mechanisms for hydroxyl radical reactions with alcohols [3]. The calculated rate constant (AOPWIN v1.89) for site 1 is  $k = 10.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , whereas the rates for sites 2–4 are each  $k = 1.41 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The faster reaction rate for site 1 is predicted based on its having the hydroxyl group attached, making it more reactive. The hydrogens at sites 2, 3, and 4 are attached to secondary carbons and



**Table I** OH + COL Reaction Product Data and Correction Factors. Reaction Channel refers to the site of H abstraction to form the product, Predicted Yield is the SAR predicted value for the reaction channel,  $k_{\text{Product}}$  is the OH + Product bimolecular rate constant,  $F_{\text{avg}}$  is the average correction factor calculated using Eq. (7) for the yield data set, and  $F_{\text{max}}$  is the largest correction factor calculated using Eq. (7) for the yield data set.

Reaction Channel	Predicted Channel Yield	Observed Product	Observed Product Yield	$k_{\text{Product}}$ ( $10^{-12}$ molecules $^{-1}$ s $^{-1}$ )	k Product Source	$F_{\text{avg}}$	$F_{\text{max}}$
1	0.60		$0.55 \pm 0.06$	6.39 12.1	Experimental [10] AOPWIN v1.89	1.04	1.12
2	0.16		$(0.32 \pm 0.15)^*$	52.2	AOPWIN v1.89	$(1.38)^*$	$(2.32)^*$
			$(0.31 \pm 0.14)^*$	40.3	AOPWIN v1.89	$(1.28)^*$	$(1.96)^*$
			No Evidence of Formation	23.8 46.9	Experimental [10] AOPWIN v1.89		
3	0.16		NEF	86.0	AOPWIN v1.89		
			NEF	75.9	AOPWIN v1.89		

3	0.16		NEF	80.4	AOPWIN v1.89	(1.28)*	(1.96)*
			(0.08 ± 0.04)*	21.1	AOPWIN v1.89	(1.14)*	(1.45)*
			No Evidence of Formation	132	AOPWIN v1.89		
4	0.08		NEF	34.5	AOPWIN v1.89		
			NEF	109	AOPWIN v1.89		
			NEF	80.4	AOPWIN v1.89		

\* Concentration data approximated using calibration curve for cyclohexanol

therefore do contribute significantly to the overall rate. Still, much lower abstraction rates for these sites are predicted because they have no groups attached directly or on the next nearest neighbor that enhance their respective hydroxyl reactivities. SAR predicts that ~60% of the hydrogen abstraction should occur at site 1. This is comparable with what is reported here in Table I for the product CON.

Subsequent reactions of the RO· radicals formed at sites 2–4 can include reaction with O<sub>2</sub>, unimolecular decomposition, and isomerization [10,11]. Previous studies have indicated that isomerization reactions of cyclohexoxy radicals are of minor or negligible importance because of the preferred chair conformation [20]. The position of the OH group relative to the radical at sites 2–4 largely determines the likelihood of oxidation or decomposition as well as the further degradation of COL.

Previous work with β-hydroxyalkoxy radicals (as formed by hydrogen abstraction at site 2) has indicated that for this class of compounds, decomposition is generally more significant than oxidation [11]. This is particularly true when the radical-leaving species has more than one carbon. For example, for the CH<sub>2</sub>CH(OH)CH(O·)CH<sub>3</sub> radical, the calculated  $k_d = 2.7 \times 10^7 \text{ s}^{-1}$  versus a calculated  $k_{O_2}[\text{O}_2] = 4.1 \times 10^4 \text{ s}^{-1}$  [11]. The predominance of decomposition is in agreement with the observance of only the product HXD from reaction site 2.

Both decomposition and oxidation should be significant pathways for the alkoxy radicals formed from abstraction at sites 3 and 4. For example, Atkinson et al. reports for the cyclohexoxy radical, the calculated  $k_d = 6.3 \times 10^4 \text{ s}^{-1}$  and  $k_{O_2}[\text{O}_2] = 2.2 \times 10^4 \text{ s}^{-1}$  [20]. The products observed in this study, 3HC and 4HC, are indicative of only the oxidation pathway. However, it can be seen from Scheme I that decomposition pathways for both of these reaction channels have multiple splits, ultimately resulting in several very reactive species (see Table I, several predicted  $k_{OH} > 70 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Therefore, the initial products from the decomposition paths may be present in concentrations beneath the detection limits of our current equipment. No secondary products of significant molecular weight were detected, and attempts to monitor smaller species such as formaldehyde or carbon monoxide provide no conclusive insight, as they are formed also during OH generation from methyl nitrite.

It is difficult to combine the yield data for CON with that of HXD, 3HC, and 4HC and derive detailed results with a high degree of confidence. However, in general it can be surmised that hydrogen abstraction occurs preferentially according to site 1  $\gg$  site 2 and

site 3  $>$  site 4. This is in agreement with SAR [8] predictions. Sites 2 and 3 are predicted to produce higher product yields than site 4 only because they have more equivalent sites.

## CONCLUSIONS

The OH + COL bimolecular rate constant,  $k_{COL}$ , was measured using the relative rate technique. A value for  $k_{COL}$  of  $(19.0 \pm 4.8) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  was determined. Using [OH] of  $1 \times 10^6 \text{ molecules cm}^{-3}$  yields an atmospheric (1/e) lifetime for COL of approximately 15 hours.

OH + COL reaction products CON ( $0.55 \pm 0.06$ ), HXD ( $0.32 \pm 0.15$ ), 3HC ( $0.31 \pm 0.14$ ), and 4HC ( $0.08 \pm 0.04$ ) were evaluated in light of the expected atmospheric reaction mechanisms. The mechanisms propose that the OH radical abstracts hydrogen from all four of the possible sites on COL. The alcoholic hydrogen (site 1) is the most active site in agreement with SAR predictions [8]. The position of the OH group relative to the alkoxy radical determines the dominant subsequent reactions (isomerization, decomposition, or reaction with O<sub>2</sub>) for sites 2–4.

## BIBLIOGRAPHY

1. Wells, J. R.; Wiseman, F. L.; Williams, D. C.; Baxley, J. S.; Smith, D. F. *Int J Chem Kinet* 1996, 28, 475.
2. Baxley, J. S.; Henley, M. V.; Wells, J. R. *Int J Chem Kinet* 1997, 29, 637–644.
3. Baxley, J. S.; Wells, J. R. *Int J Chem Kinet* 1998, 30, 745–752.
4. Markgraf, S. J.; Semple, J.; Wells, J. R. *Int J Chem Kinet* 1999, 31, 315–322.
5. Wyatt, S. E.; Baxley, J. S.; Wells, J. R. *Int J Chem Kinet* 1999, 31, 551–557.
6. Wyatt, S. E.; Bradley, W. R.; Wells, J. R. Manuscript in preparation.
7. Markgraf, S. J.; Wells, J. R. *Int J Chem Kinet* 1997, 29, 445–451.
8. Kwok, E. S. C.; Atkinson, R. *Atmos Environ* 1995, 29, 1685.
9. Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 3rd ed.; Allyn and Bacon: Boston, MA, 1973; p 286.
10. Atkinson, R. *J Phys Chem Ref Data*, Monograph No. 2, 1994.
11. Atkinson, R. *Int J Chem Kinet* 1997, 29, 99–111.
12. Atkinson, R.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J Air Pollut Control* 1981, 31, 1090.
13. O'rji, L. N.; Stone, D. A. *Int J Chem Kinet* 1992, 24, 703.
14. Williams, D. C.; O'rji, L. N.; Stone, D. A. *Int J Chem Kinet* 1993, 25, 539.

15. Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; Bufalini, J. J. *Int J Environ Anal Chem* 1994, 54, 265.
16. Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int J Chem Kinet* 1995, 27, 453.
17. Atkinson, R.; Aschmann, S. M.; Carter, W. P. L.; Winer, A. M.; Pitts, J. N., Jr. *J Phys Chem* 1982, 86, 4563.
18. Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E. *J Chromatogr* 1989, 483, 431.
19. Taylor, W. D.; Allston, D.; Moscato, M. J.; Fazekas, G. D.; Kozlowski, R.; Takacs, G. A. *Int J Chem Kinet* 1980, 12, 231.
20. Atkinson, R.; Aschmann, S. M.; Chew, A. A.; Arey, J. *J Phys Chem* 1997, 101, 8042.
21. Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int J Chem Kinet* 1995, 27, 453.
22. Smith, D. F.; Kleindienst, T. E.; Hudgens, E. E.; McIver, C. D.; Bufalini, J. J. *Int J Chem Kinet* 1992, 24, 199.
23. Wallington, T. J.; Andino, J. M.; Potts, A. R.; Rudy, S. J.; Siegl, W. O.; Zhang, Z.; Kurylo, M. J.; Huie, R. E. *Environ Sci Technol* 1993, 27, 98.
24. Veillerot, M.; Foster, P.; Guillermo, R.; Galloo, J. C. *Int J Chem Kinet* 1996, 28, 235.
25. Dagaut, P.; Wallington, T.; Liu, R.; Kurylo, M. *J Phys Chem* 1988, 92, 4375.